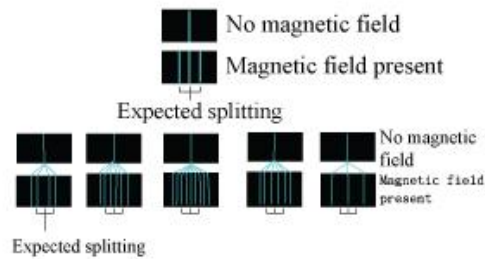# 【Chapter 7 Electron Spin】

【7.1 Electron Spin】

Figure 7.1 (see textbook)The normal and anomalous Zeeman effects in various spectral lines.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum

Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

＊Fine structure：many spectral lines consist of two separate lines that are very close to each other.

ex. H atom, first line of Balmer series

n = 3 → n = 2 => 656.3nm

in reality, two lines separate 0.14nm

Zeeman Effect：

From chapter 6, spectral lines of an atom in a magnetic field

→ split into 3 components.

In reality, more components were observed. Anomalous Zeeman Effect are shown in Fig 7.1

⇨ Every electron has an intrinsic angular momentum, called spin, whose magnitude is the same for all e'. Associated with this angular momentum is a magnetic moment (proposed by Goudsmit & Ohlenbeck)

Classical picture：
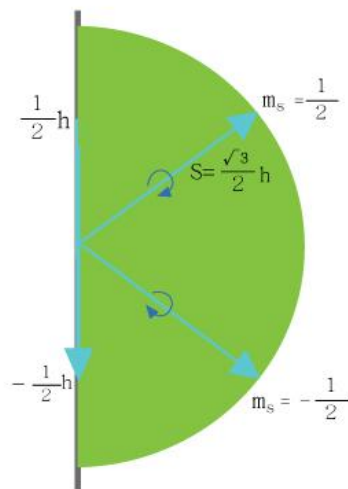
Figure 7.2 (see textbook) The two possible orientations of the spin angular-momentum vector are "spin up" (ms = +$\frac{1}{2}$) and "spin down" (ms = -$\frac{1}{2}$)

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

spins → an electron as a charged sphere spining on its axis.

The rotation involves angular momentum → magnetic moment opposite to S(angular moment)

∵ negative charge

electron spin → solve fine structure & anomalous Zeeman Effect

*From this picture, in order to have observed angular momentum associate with electron spins => e' have to rotate with an equatorial velocity $> C$ (see ex 7.1)

=>Paul Dirac in 1929 found e' must have intrinsic angular momentum & magnetic momentum

$$s = \frac{1}{2} \qquad\qquad => S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

spin quantum number $\qquad$ angular momentum due to e' spin

*Space quantization of e' $\rightarrow$ m_s(spin magnetic quantum number)

$$2s+1=2 \qquad \text{orientations} => \begin{cases} m_s = +\frac{1}{2} & \text{spin up} \\ \\ m_s = -\frac{1}{2} \end{cases}$$

$$S_z = m_s\hbar = \pm\frac{1}{2}$$

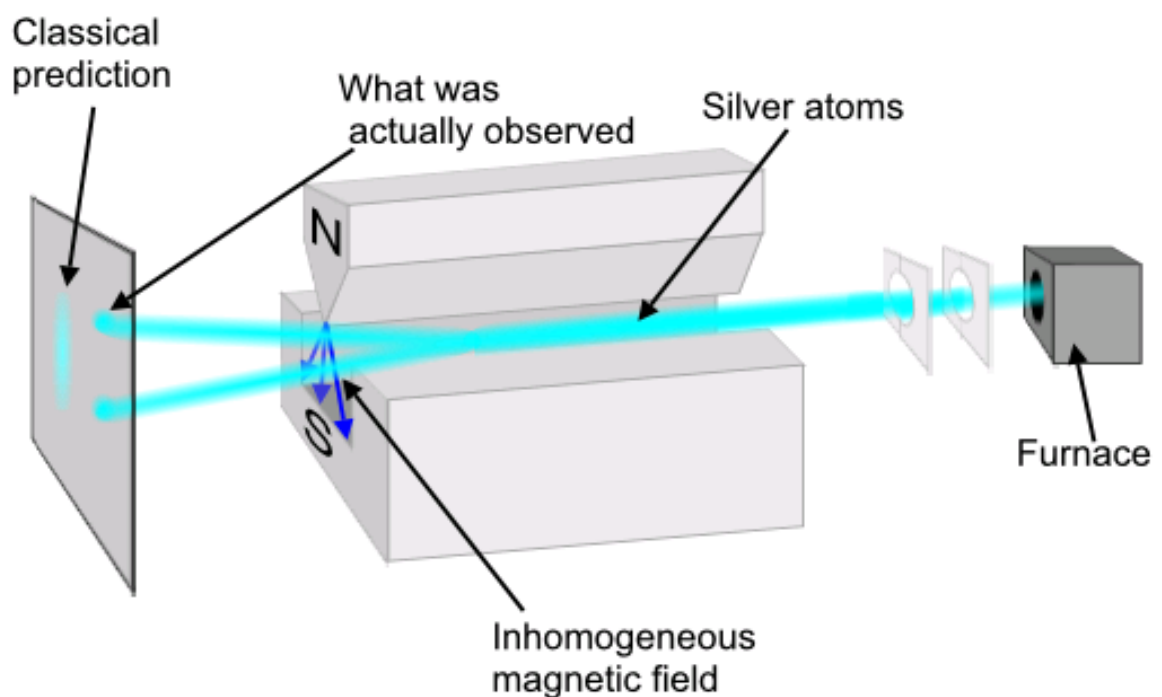spin magnetic moment $\vec{u}_s = \frac{-e}{m}\vec{S}$ (gyromagnetic ratio=2 for e' spin)

$$u_{sz} = \pm\frac{e\hbar}{2m} = \pm u_B$$

Stern & Gerlach found the initial beam split into two

distinct parts that correspond to the two opposite spin orientations in the magnetic field permitted by space quantization.

⇨ A total of four quantum numbers are needed to describe each possible state of an e'

$$n, \ell, m_\ell, \& m_s$$

Figure 7.3 The Stern-Gerlach experiment (source: wikipedia)

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick
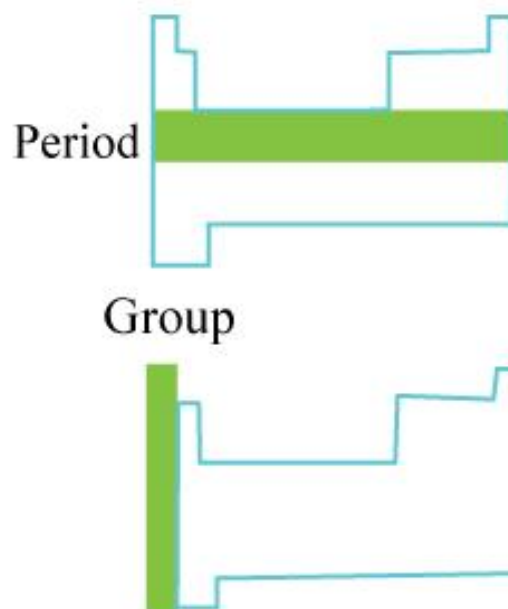
【7.2 Exclusion Principle】

For elements that have atomic number 9(F),10(Ne),11(Na)

⇨ chemically different

If all e' in an atom were in the same quantum state => no way

that chemical properties of elements change so sharply.

*Pauli exclusion principle

No two electrons in an atom can exist in the same quantum

state. Each e' must have a different set of quantum

number n, ℓ, m_ℓ, m_s.

Figure 7.4 (see textbook) The elements in a group of the periodic table have similar properties, while those in a period have different proper- ties.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

【7.3 Symmetric & antisymmetric Wave Function】

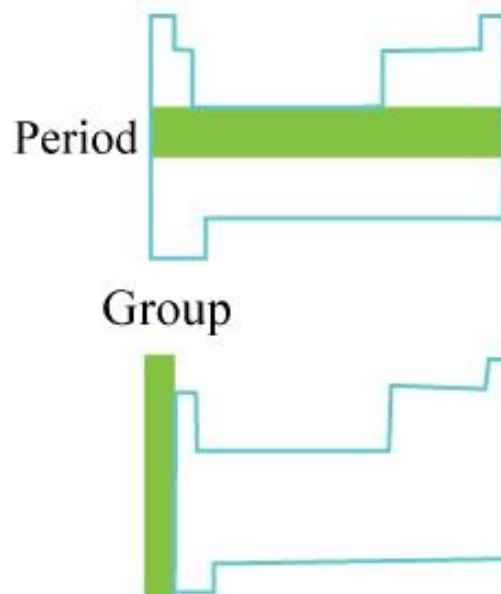Complete wave function $\varphi(1,2,3,...,n)$ of a system of n noninteracting particles can be expressed as

$$\varphi(1,2,3,...,n) = \varphi(1)\varphi(2)\varphi(3)...\varphi(n)$$

＊Consider two identical particles case. One in quantum state a, the other in quantum state b.

∵particles are identical

⇨ $|\varphi|^2$ are the same if particles ate exchanged.

⇨ $|\varphi|^2(1,2) = |\varphi|^2(2,1)$

Figure 7.4 (see textbook) The elements in a group of the periodic table have similar properties, while those in a period have different properties.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

symmetric $\qquad \varphi(2,1) = \varphi(1,2)$

antisymmetric $\qquad \varphi(2,1) = -\varphi(1,2)$

If particle 1 is in state a, and particle 2 is in state b, the wave function of the system is

$$\varphi_I = \varphi_a(1)\varphi_b(2)$$

If particle 2 is in state a, and particle 1 is in state b,

$$\varphi_{II} = \varphi_a(2)\varphi_b(1)$$

$\because$ two particles are indistinguishable => no way to know whether φ_I or φ_{II} describes the system.

The probability for $\varphi_I = \varphi_{II}$

$\Rightarrow$ system spends half the time in configuration whose wave function is φ_I and the other half is φ_{II}

$\Rightarrow$ a linear combination of φ_I & φ_{II} is the proper description of the system.

Symmetric $\quad \varphi_s = \dfrac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)]$

Antisymmetric $\quad \varphi_A = \dfrac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)]$

$\dfrac{1}{\sqrt{2}}$ is needed for normalization.

In symmetric case, both particles 1 & 2 can simultaneously exist in the same state with a=b but in the antisymmetric case, if a=b

$$\Rightarrow \varphi_A = \frac{1}{\sqrt{2}} \left[\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1) \right] = 0$$

$\Rightarrow$ Two particles can not be in the same quantum state.

Pauli found that no two e' in an atom can be in the same quantum state.

$\Rightarrow$ systems of e' are described by wave function that reverse sign upon the exchange of any pair of them.

*Experiments show that all particles which have odd half-integral spins $\left(\frac{1}{2}, \frac{3}{2}, ... \right)$ have wave functions that are antisymmetric to an exchange of any pair of them.

$\Rightarrow$ includes protons & neutrons & e'

$\Rightarrow$ obey exclusion principle

$\Rightarrow$ particles of odd half-integral spin are referred to as fermions (obey Fermi-Dirac distribution)

*Particles whose spins are 0 or integer have functions that are symmetric to an exchange of any pair of them.

⇨ include photons, α particles, Helium atoms

⇨ do not obey exclusion principle

⇨ particles of 0 or integral spin are often referred to as bosons (obey Bose-Einstein distribution)

Many-Electron

E

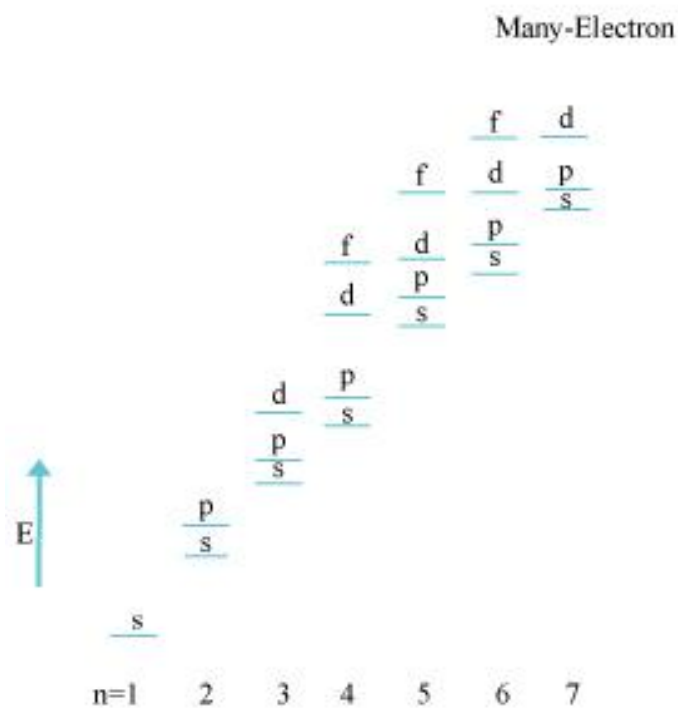|				f	d	
			f	d	p	
					s	
				p		
		f	d	s		
		d	p			
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n=1   2   3   4   5   6   7

Figure 7.12 The sequence of quantum states in an atom. Not to scale.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

＊Spin-orbit Coupling

◆Fine-structure doubling of spectral lines arises from a magnetic

interaction between the spin & orbital angular momenta.

◆An e' revolving about a nucleus finds itself in a magnetic field

→ magnetic field acts on e' spin magnetic moment to produce a

kind of internal Zeeman Effect.

$$u_m = -uB\cos\theta = -u_z B = \pm u_B B$$

◆Depending on the orientation of its spin vector, the E will be

higher of lower by $u_B B$ than its energy without spin-orbit

coupling.

⇨ Every quantum state (except s states $(\ell = 0)$) is split into

two substates.
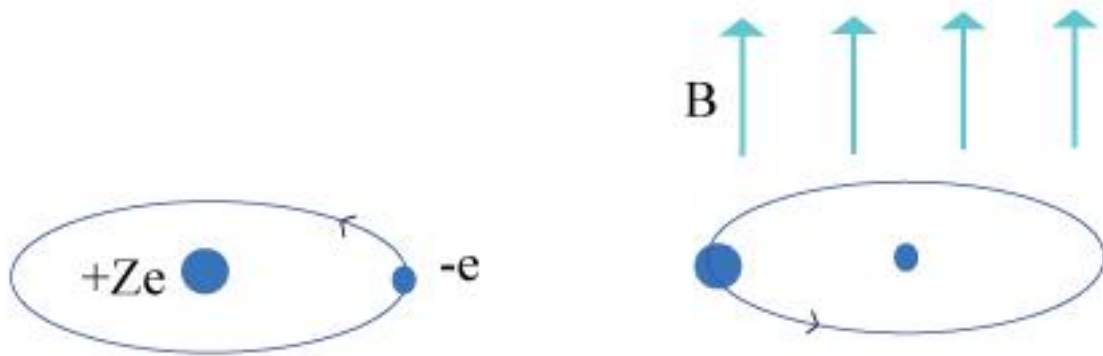
Figure 7.13 (see textbook) (a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b)From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the orbit. The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

Example 7.3

Estimate the magnetic energy U_m for an e' in the 2p state of a hydrogen atom using the Bohr model, whose n=2 state corresponds to 2p state.

Sol：

$$B = \frac{u_0 I}{2r}$$

The orbiting e' sees itself circled f times per second by the proton of charge +e that is nucleus,
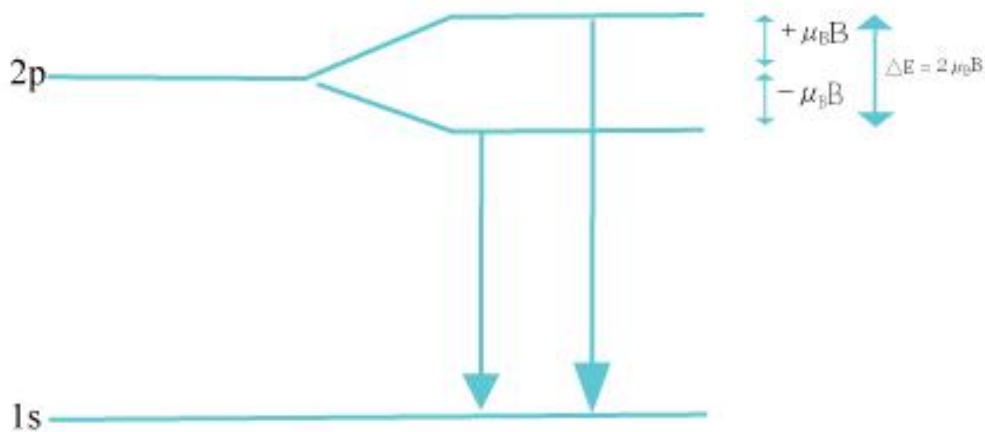
$$\Rightarrow B = \frac{u_0 fe}{2r}$$

$$f = \frac{v}{2\pi r} \text{ and } r = n^2 a_0$$

$$B = \frac{4\pi \times 10^{-7} \times \left(8.4 \times 10^{14} s^{-1}\right)\left(1.6 \times 10^{-19} C\right)}{2 \cdot \left(2.1 \times 10^{-10} m\right)}$$

$$U_m = u_B B = \left(9.27 \times 10^{-24}\right) J/T \times 0.4 T$$

$$= 3.7 \times 10^{-24} \text{ J} = 2.3 \times 10^{-5} \text{ eV}$$

Figure 7.14 (textbook) Spin-orbit coupling splits the 2*p* state in the hydrogen atom into two substates Δ *E* apart. The result is a doublet (two closely spaced lines) instead of a single spectral line for the 2*p* →1*s* transition.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick
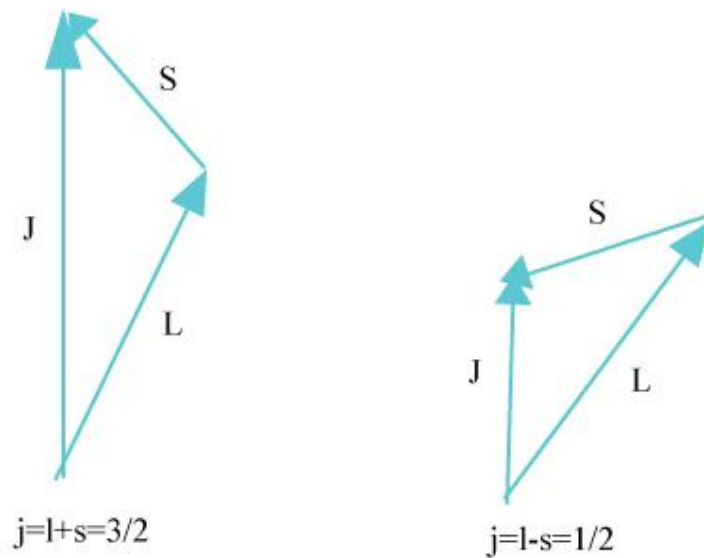
◆Total angular momentum

◆For atoms with single electron $\vec{J} = \vec{L} + \vec{S}$

$$J = \sqrt{j(j+1)}\hbar \qquad j = \ell + s = \ell \pm \frac{1}{2} \qquad J_z = m_j \hbar, \quad m_j = -j, \ldots j$$
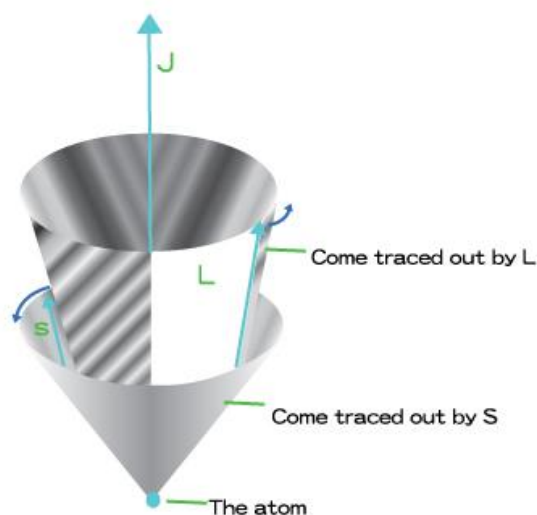
◆For $\vec{J}, \vec{L}, \vec{S}$, both magnitude & direction are quantized for atoms with single e' $\quad j = \ell + s \quad \Rightarrow J>L$

$\vec{L} \& \vec{S}$ can never be exactly parallel or antiparallel to each other or to $\vec{J}$.

j=l+s=3/2   j=l-s=1/2

Figure 7.15 (see textbook) The two ways in which **L** and **S** can be added to form J when $l = 1$, $s = 1/2$.
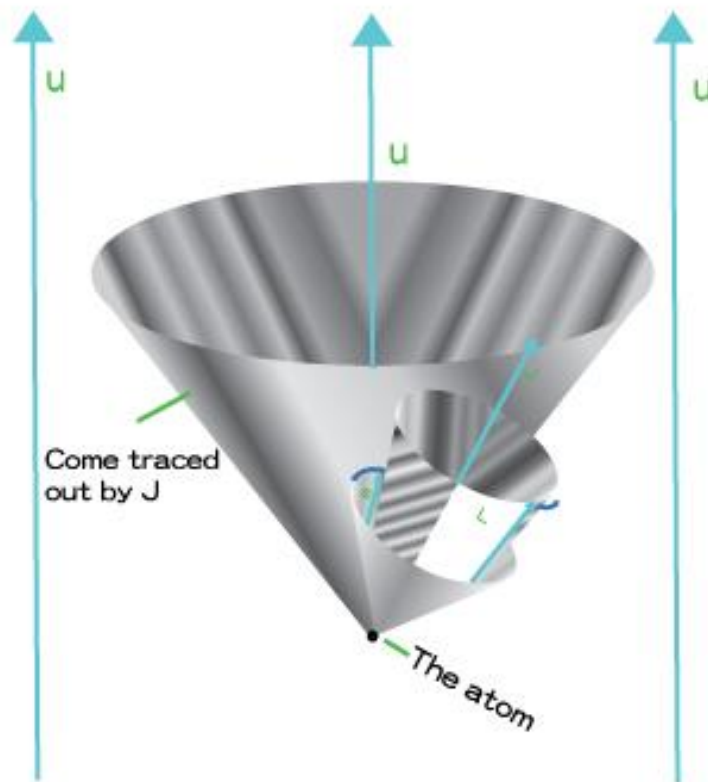
Figure 7.16 (see textbook) Space quantization of total angular momentum when the orbital angular momentum is $l = 1$.

Figure 7.17 (see textbook) The orbital and spin angular-momentum vector **L** and **S** precess about **J**.

＊ $\vec{L}\,\&\,\vec{S}$ interact magnetically. If no external field => $\vec{L}\,\&\,\vec{S}$ precess around J

Figure 7.18 (see textbook) In the presence of an external magnetic field **B**, the total angular-momentum vector **J** precesses about **B**.

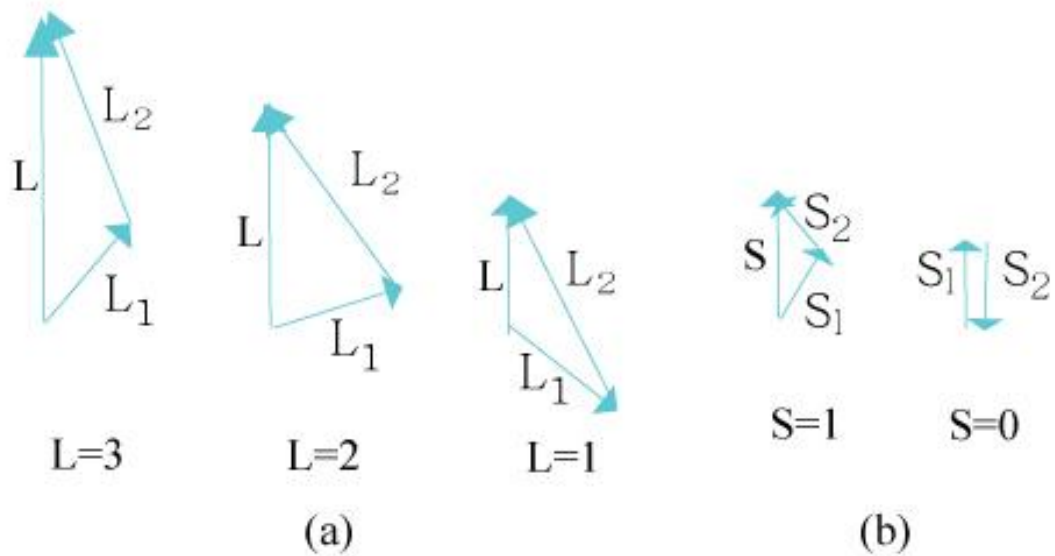※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

＊ If B present => J process about B, while L & S still continue processing about J. The precession of J about B is what give rise to the anomalous Zeeman Effect, since different orientation of J involves slightly different energies in the presence of B.

Figure 7.19 (see textbook) When $l_1 = 1$, $s_1 = \frac{1}{2}$. and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which $\mathbf{L}_1$ and $\mathbf{L}_2$ can combine to form $\mathbf{L}$ and two ways in which $\mathbf{S}_1$ and $\mathbf{S}_2$ can combine to form $\mathbf{S}$.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

● LS Coupling

When more than one e' contributes orbital & spin angular momenta to the total angular momentum J of an atom, J is still the vector sum of these individual momenta.

Orbital angular momenta L_i of various e' are coupled together into a single resultant L. Same for S_i

$$=> \vec{L} = \sum \vec{L}_i$$

$$\vec{S} = \sum \vec{S}_i$$

The momenta $\vec{L} \& \vec{S}$ interact via spin-orbit effect to form a total angular momentum J => LS coupling

$$\vec{J} = \vec{L} + \vec{S}$$

$$L = \sqrt{L(L+1)}\hbar$$

$$L_z = M_l \hbar$$

$$S = \sqrt{S(S+1)}\hbar$$

$$S_z = M_s \hbar$$

$$J = \sqrt{J(J+1)}\hbar$$

$$J_z = M_j \hbar$$

*L & M_L are always integers or 0

*other quantum numbers are half-integral if an odd number

of e' is involved and integral or 0 if an even number of e'

is involved.

*J range from $|L - S|$ to L+S

⇨ when L>S, J can have 2s+1 values

⇨ when L<S, J can have 2L+1 values

Example 7.5

Find the possible values of the total angular-momentum

quantum number J under LS coupling of two atomic e' whose

orbital quantum number are $\ell_1 = 1$ & $\ell_2 = 2$.

Sol：

See fig 7.19

$\bar{L} = \bar{L}_1 + \bar{L}_2$ all values of L are possible from $\left| \ell_1 - \ell_2 \right|$ to

$$\ell_1 + \ell_2$$

∴L=1,2,3.

The spin quantum number s is always $\dfrac{1}{2}$

S=1,0.

J can have any value between $\left| L - S \right|$ to L+S

J=0,1,2,3,4.

Term Symbols

Total angular-momentum quantum number L

L = 0, 1, 2, 3, 4, 5, 6
    s p D F G H I

A superscript number before the letter (^{2}p, for example) is used to indicate the multiplicity of the state, which is the number of different possible orientations of **L** and **S**, and hence the number of different possible value of **J**. The multiplicity is equal to 2s+1 for **L**>**S**, and is equal to 2L+1 for **S**>**L**.

- For **L>S** case

  If s =0 => multiplicity is 1 (singlet state) **J=L**

  If s = $\frac{1}{2}$ => multiplicity is 2 (doublet state) $J = L \pm \frac{1}{2}$

  If s =1 => multiplicity is 3 (triplet state) J=L+1,L,L-1

- The total angular-momentum quantum number J is used as a

  subscript after the letter

  => $^2 p_{\frac{3}{2}}$ (doublet p three-halves)

  $$S = \frac{1}{2}, \text{L=1},\ J = \frac{3}{2}$$

In the event that the angular momentum of the atom arises from

a single outer e' => principle quantum number n is used as a

prefix.

Ground state of sodium => $3^2 s_{\frac{1}{2}}$

$\Rightarrow n = 3, \ell = 0, s = \frac{1}{2}, j = \frac{1}{2}$

It is conventional to denote the above state by $3^2 s_{\frac{1}{2}}$ with 2

indicating a doublet, even though there is only a single

possibility for J (∵ L=0)

Example 7.6

For $3^2 s_{\frac{1}{2}}$ & $3^2 p_{\frac{1}{2}}$ list possible quantum number n, ℓ, j, m_j

fof the outer e'

Sol：$3^2 s_{\frac{1}{2}}$：$n = 3, \ell = 0, j = \dfrac{1}{2}, m_j = \pm \dfrac{1}{2}$

$3^2 p_{\frac{1}{2}}$：$n = 3, \ell = 1, j = \dfrac{1}{2}, m_j = \pm \dfrac{1}{2}$
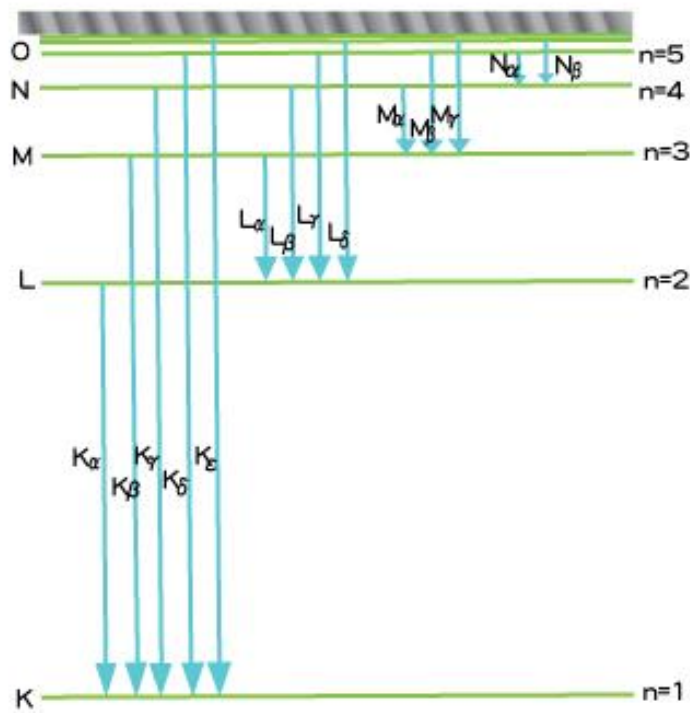

Figure 7.20 (see textbook) The origin of x-ray spectra.

For k_α L electron drops to K state.

The L electron experiences a nuclear charge of Ze that is

reduced to an effective charge in the neighborhood of (Z-1)e by

the shielding effect of the remaining k e'

$$=> \nu = \frac{m(z-1)^2 e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)= CR(z-1)^2\left(\frac{1}{1^1}-\frac{1}{2^2}\right)$$

$$\nu = \frac{3CR(z-1)^2}{4} \qquad => E(k_\alpha)= (10.2eV)(z-1)^2$$

$$R=1.07\times10^7 \text{ m}^{-1}$$